Effect of optical excitation energy on the red luminescence of Eu^{3+} in GaN

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Photoluminescence (PL) excitation spectroscopy mapped the photoexcitation wavelength dependence of the red luminescence ($^5D_0 \rightarrow {}^7F_2$) from GaN:Eu. Time-resolved PL measurements revealed that for excitation at the GaN bound exciton energy, the decay transients are almost temperature insensitive between 86 K and 300 K, indicating an efficient energy transfer process. However, for excitation energies above or below the GaN bound exciton energy, the decaying luminescence indicates excitation wavelength- and temperature-dependent energy transfer influenced by intrinsic and Eu^{3+}-related defects. © *2005 American Institute of Physics*.
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Rare earth-doped (RE) III-V semiconductors are promising materials for visible wavelength emitters because their very sharp linewidths are much less sensitive to host and temperature than their quantum well and quantum dot counterparts. Among the various hosts, GaN is appealing because its direct wide band gap allows visible wavelength emission while providing great chemical and physical stability. Visible wavelength emission from GaN:Er,[1] GaN:Tb,[2] GaN:Pr,[3] GaN:Eu,[4] and GaN:Tm[5] has already been demonstrated.

Native and rare earth-induced defects participate in the energy transfer processes that lead to red light emission in GaN:Eu.[6] An impurity band spreading 370 meV below the conduction band of GaN:Eu has been observed to arise from such defects.[7] Previous measurements of the extended x-ray absorption fine structure show that Er^{3+} and Eu^{3+} dopants assume a substitutional Ga site with C_{3v} symmetry.[8,9] Sharp, otherwise forbidden $4f$ emission lines from Eu^{3+} are allowed by symmetry breaking in the GaN host. Nyein *et al.* recently performed time-resolved photoluminescence (PL) studies of these emission lines by using both above-and below-band gap excitation.[10] Photoluminescence excitation (PLE) spectroscopy indicated the impurity band is involved in the energy transfer between the GaN host and the Eu^{3+} dopants. In this paper, visible and UV wavelength PLE measurements of GaN:Eu evaluate the excitation wavelength-dependent energy transfer between the GaN host or defects and the Eu^{3+} dopants, while temperature-dependent, time-resolved PL (TRPL) measurements investigate energy transfer and carrier relaxation dynamics.

A Eu-doped GaN film was deposited on a p-Si (111) substrate by solid-source MBE. A thin GaN buffer layer was first deposited at a substrate temperature of 600 °C before the main growth took place at 800 °C for about 2 h. Details of the growth conditions can be found elsewhere.[4] The Eu cell temperature was 400 °C, resulting in a Eu concentration of 8.8×10^{20} cm^{-3} (1 at. %) estimated by secondary ion mass spectrometry. The thickness of the GaN:Eu layer is approximately 2.4 μm. PL spectra were excited by a He–Cd laser (E_p=3.815 eV), and the tunable light source for PLE spectroscopy was a xenon arc lamp dispersed through an Acton 150 mm monochromator. The luminescence was analyzed by a 0.75 m focal length SPEX single grating monochromator and detected by a thermoelectrically cooled photomultiplier tube (Hamamatsu R928). Standard lock-in techniques were used for collecting both PL and PLE signals. The pulsed laser source for TRPL measurements was an optical parametric amplifier (OPA), pumped by a 1 kHz regenerative amplifier seeded by an 80 MHz Ti:sapphire oscillator operating at 800 nm. In this experiment the OPA was tuned between E_p =3.02–4.14 eV while maintaining a pulse intensity of 600 $\mu J/cm^2$ and pulse width less than 200 fs. The luminescence from the GaN:Eu sample was collected by two UV lenses, spectrally and temporally dispersed by an electronic streak camera (Hamamatsu C4334) with 0.16 nm and 2.1 μs resolution, respectively.

Photoluminescence from $^5D_0 \rightarrow {}^7F_3$ (1.870 eV), $^5D_0 \rightarrow {}^7F_2$ (1.992 eV), and $^5D_0 \rightarrow {}^7F_1$ (2.064 eV) are evident in Fig. 1(a). The weak yellow luminescence centered at 2.3 eV and the strong donor–acceptor pair (DAP) luminescence[11,12] at 3.263 eV, with its 92-meV LO-phonon replica at 3.171 eV, are observed at 86 K but not at 300 K. The yellow luminescence indicates the presence of native GaN defects or impurity levels unrelated to the Eu-induced traps.

To investigate the wavelength-dependent excitation efficiency of the $^5D_0 \rightarrow {}^7F_2$ transition, PLE spectroscopy was carried out in the 2.067–4.428 eV spectral range. The bandpass of the spectrometer was set at 5.6 nm to monitor the entire ~2.5 nm linewidth of the transition. The resulting PLE spectra at 86 K and 300 K [Fig. 1(b)], normalized by the incident beam intensity, exhibit strong UV absorption bands that indicate efficient transfer of excitation from the GaN host to the $^5D_0$ state of Eu^{3+}, especially at 86 K. The prominent I_2 bound exciton peak, corresponding to shallow donors,[13] was observed to shift with the GaN band edge 85 meV from E_X=3.473 eV at 86 K to 3.388 eV at 300 K. Below the GaN band edge, a >400 meV-wide absorption tail that falls off dramatically with decreasing energy indicates that traps and defect levels may also transfer excitation

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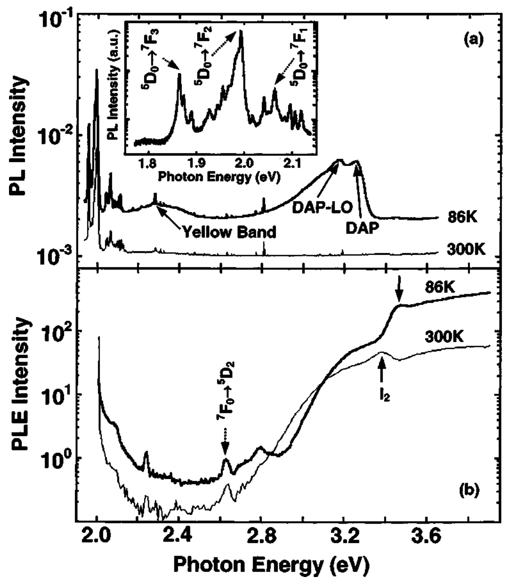

FIG. 1. (a) The PL spectra (E_p=3.815 eV) of GaN:Eu at 86 K and 300 K. The inset PL spectrum was obtained by below-gap excitation (E_p=3.1 eV) at 300 K. (b) PLE spectra for the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} in wurtzite GaN. The solid arrows indicate the shift of the I_2 bound exciton line with temperature.

to Eu^{3+}, in agreement with recent observations.[10,14] Note also that the DAP feature in the PL spectrum of Fig. 1(a) closely matches the observed broad PLE absorption tail identified in Fig. 1(b), further suggesting that these shallow states are involved in the energy transfer between GaN host and RE ions. Indeed, as shown in the inset of Fig. 1, a weaker but otherwise characteristic photoluminescence of Eu^{3+} dopants was observed using below-gap excitation into the DAP feature.

Because of the large size of the RE dopants, Eu doping of GaN generates a high density of native defects, especially shallow donor nitrogen vacancies near Eu^{3+} seen as I_2 bound excitons.[13,15] The Eu^{3+} dopants and nearby native defects can interact with each other, forming a variety of complexes which enhance formation of bound excitons and facilitate energy transfer between native traps and Eu^{3+} dopants. Pump wavelength-dependent TRPL measurements were performed to study the temperature-dependent carrier relaxation dynamics from the GaN host or defects to the Eu^{3+} dopants. Examples of normalized TRPL decay for a 2.5-nm-wide window centered on the $^5D_0 \rightarrow {}^7F_2$ transition are shown in Fig. 2. Because of the temperature-dependent shift of E_X, E_p was

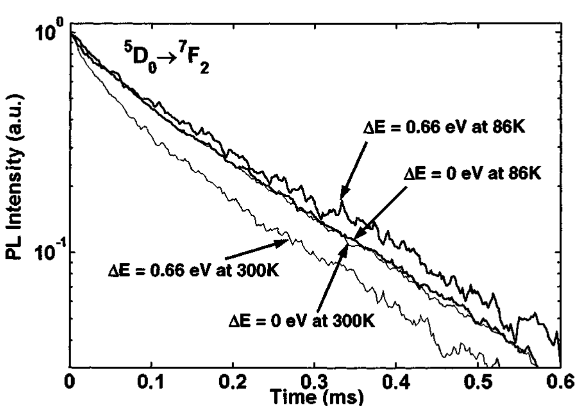

FIG. 2. TRPL decay transients monitored at 86 K and 300 K for the $^5D_0 \rightarrow {}^7F_2$ transition in GaN:Eu following photoexcitation at ΔE=0 and 0.66 eV.

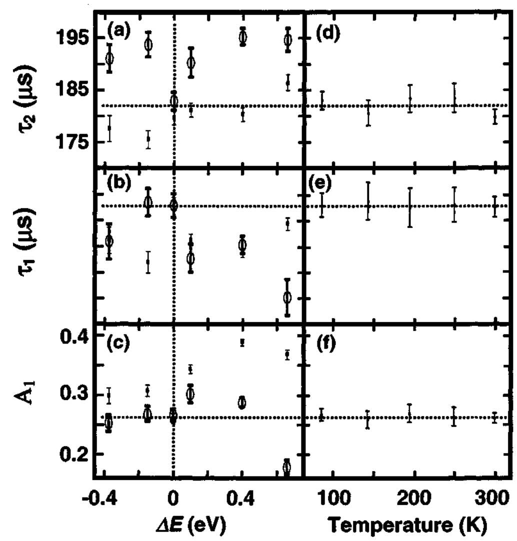

FIG. 3. (a)–(c) Behavior of the slow (τ_2) and fast (τ_1) decay constants and the amplitude of the fast decaying component (A_1) as a function of ΔE at 86 K (○) and 300 K (■). (d)–(f) Similar data as a function of temperature for ΔE=0. Dotted lines indicate the average ΔE=0 values.

adjusted at each temperature so that TRPL decay could be compared for a given $\Delta E = E_p - E_X$. All TRPL data were fit with a bi-exponential equation $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. The fast ($\tau_1$) and slow ($\tau_2$) decay constants, and the relative strength of the amplitude normalized ($A_1 + A_2 = 1$) fast decaying component (A_1), are plotted as a function of ΔE in Figs. 3(a)–3(c).[16]

It is quickly noticed that photoexcitation at any energy $\Delta E \neq 0$ produces different relaxation behavior at 86 K than at 300 K. The greater $|\Delta E|$ is, the greater are the differences in the relaxation behavior. The slower decay constant τ_2 is always faster, and A_1 is always larger, at 300 K than that at 86 K. Surprisingly, when photoexciting directly into the bound exciton I_2 line (ΔE=0), the decay curves, rate constants, and relative amplitudes are nearly identical at all temperatures [Figs. 3(d)–3(f)]. These observations indicate a very efficient energy transfer pathway between the bound I_2 exciton and the Eu^{3+} dopants that decreases in effectiveness when photoexcited carriers are generated at other energies.

Nonradiative relaxation involving native and Eu-related defects appears to be responsible for this. Although the slow component is dominated by $^5D_0 \rightarrow {}^7F_2$ radiative decay, it has recently been shown that both decay components include contributions from the nonradiative exchange of excitation between Eu^{3+} dopants and host impurities.[6] For photoexcitation by 4.13 eV pulses ($\Delta E \sim 0.7$ eV), it was posited that the impurities acted as a reservoir that depleted and repopulated the $^5D_0$ state in a temperature-dependent manner characterized by a thermal activation barrier of 16 meV. The role these impurities play is evident in the below band gap PLE absorption feature [Fig. 1(b)], which arises from the nonradiative energy transfer out of these native traps and eventually into the $^5D_0$ state. Further proof is found in the absence of 300 K DAP emission, as well as the below bandgap DAP emission [Fig. 1(a)] which was measured to decay in ~410 ps at 86 K. By contrast, DAP emission decay for undoped and Mg-doped GaN (~1 μs and ~100 ns, respectively)[17,18] occurs much more slowly, indicating the existence of competing, nonradiative decay channels in GaN:Eu.

The ΔE dependence revealed in Figs. 3(a)–3(c) provides more insight into these nonradiative relaxation processes. The temperature-insensitive behavior observed for photoexcitation at $\Delta E=0$ suggests that Eu complexes act as shallow donors in GaN and that I_2 excitons are bound to these sites. Temperature-insensitive, Auger-mediated transfer of excitation to the $4f$ levels of Eu^{3+} occurs efficiently for excitons photoexcited at that energy. Photoexcitation at other energies ($\Delta E \neq 0$) generates free excitons and excitons trapped by defect complexes with various energy levels and storage lifetimes. Because intrinsic GaN radiative recombination depletes free excitons in $\sim$1 ns,[19] the most important energy transfer mechanism on the microsecond time scale appears to be a thermally activated hopping of bound excitons from trap to trap. Eventually the exciton is bound to a Eu^{3+} site and the aforementioned Auger process transfers excitation to the $4f$ levels. The increasing importance of this pathway is evident in Fig. 3(c), which indicates that the role of traps and other nonradiative pathways[19] is always larger at 300 K than at 86 K in a manner that increases in importance with increasing $|\Delta E|$. Intuitively stated, thermally activated percolation of excitons from site to site grows more effective in finding Eu^{3+} sites with increasing temperature and decreasing $|\Delta E|$. This hypothesis is corroborated by Fig. 3(a) in which τ_2 at 86 K is slower than at 300 K for every E_p except $\Delta E=0$.

In conclusion, visible and UV PLE measurements have been performed for the $^5D_0 \rightarrow {}^7F_2$ transition in GaN:Eu. Strong absorption occurs at pump energies above the GaN band gap, while a broad impurity band is observed below the band edge. Optical excitation into this impurity band reveals a weaker but otherwise characteristic red luminescence from the Eu^{3+} dopants, suggesting that a complex of Eu-related and native defects exist that permit energy transfer from the host and impurity bands to the $^5D_0$ state of Eu^{3+}. Pump wavelength-dependent TRPL revealed that photoexcitation at the I_2 bound exciton exhibits temperature-independent energy transfer, while photoexcitation at other energies activates additional temperature-sensitive pathways. In particular, it is suggested that photoexcitation at the I_2 exciton energy bypasses most impurity traps otherwise active when photoexcitation is above or below the GaN band gap. These results are anticipated to be ubiquitous in the RE-doped GaN system and may reconcile recent inconsistent reports of thermal quenching when the role of differing photoexcitation energies is re-examined.[10,20,21]

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